PROPERTIES OF PURE REFRIGERANTS
AND REFRIGERANT MIXTURES FROM CUBIC EQUATIONS OF STATE

Viorel FEROIU[*] and Dan GEANĂ

Department of Applied Physical Chemistry and Electrochemistry, Fac. Applied Chemistry and Material Science,
"Politehnica" University Bucharest, 1-7 Gh. Polizu Street, 011061, S1, Bucharest, Roumania

Vapour-liquid equilibrium, thermodynamic and volumetric properties were predicted for three pure hydrofluorocarbons (R32, R125 and R134a) as well as for binary and ternary mixtures of these refrigerants. Five cubic equations of state; GEOS3C (general cubic equation of state with 3 constants), SRK (Soave – Redlich – Kwong), PR (Peng – Robinson), SW (Schmidt-Wenzel) and C-1 (Freze *et al.*) were used. A wide comparison with literature experimental data was made. For the refrigerant mixtures, classical van der Waals mixing rules without interaction parameters were used. The GEOS3C equation, with three pure component parameters estimated by matching several points on the saturation curve (vapour pressure and corresponding liquid volumes), compares favorably to other equations in literature, resting simple enough for applications.

INTRODUCTION

Refrigerants are the working fluids in refrigeration, air-conditioning and heat pumping systems. Accurate knowledge and prediction of the thermo-physical properties of pure refrigerant and mixtures containing hydrofluorocarbons (HFC's), which are proposed as alternative refrigerants, is of great importance to evaluate the performance of refrigeration cycles and to determine the optimum composition of new working fluids. The development of models for representation and prediction of physical properties and phase equilibria as well as the improvement of current equations of state is of particular interest for the refrigeration industry.[1-4]

The difluoromethane (R32), pentafluoroethane (R125) and 1,1,1,2 – tetrafluoroethane (R134a) are environmentally acceptable refrigerants (their ozone depletion potentials are zero) and present a considerable interest in the search for alternative refrigerants. In previous works[5-8], some properties of pure refrigerant and refrigerant mixtures were calculated by cubic equations of state.

The purpose of this work is to present new results of simultaneous vapour-liquid equilibrium, thermodynamic and volumetric properties prediction on R32, R125, and R134a pure fluids as well as on binary and ternary mixtures of these refrigerants. Five cubic equations of state GEOS3C,[5,9,10] SRK (Soave – Redlich – Kwong),[11] PR (Peng – Robinson),[12] SW (Schmidt-Wenzel)[13] and C-1 (Freze *et. al*)[14] are used. A wide comparison with recommended literature data[15] and experimental data[16-18] is made. For the refrigerant mixtures, classical van der Waals mixing rules without interaction parameters are used.

The GEOS3C equation has three pure component parameters estimated by matching several points on the saturation curve (vapor pressure and corresponding liquid volumes). Three

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[*] Corresponding author: v_feroiu@chim.upb.ro

points on the saturation curve is the minimum number of data necessary to obtain the GEOS3C parameters. So far GEOS3C compares favorably to other equations in literature, and is simple enough for applications.

THE GEOS3C EQUATION OF STATE

The general cubic equation of state (GEOS) has the form:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V-d)^2 + c} \qquad (1)$$

The four parameters a, b, c, d for a pure component are expressed by:

$$a = a_c \, \beta^2(T_r); \quad a_c = \Omega_a \frac{R^2 T_c^2}{P_c}; \quad b = \Omega_b \frac{RT_c}{P_c};$$

$$(2)$$

$$c = \Omega_c \frac{R^2 T_c^2}{P_c^2}; \quad d = \Omega_d \frac{RT_c}{P_c};$$

For GEOS3C equation,[5,7] the temperature function used is:

$$\beta(T_r) = 1 + C_1 y + C_2 y^2 + C_3 y^3 \text{ for } T_r \le 1 \quad (3)$$

$$\beta(T_r) = 1 + C_1 y \quad \text{for } T_r > 1 \qquad (4)$$

$$y = 1 - \sqrt{T_r} \qquad (5)$$

Setting four critical conditions,[9] the expressions of the parameters Ω_a, Ω_b, Ω_c, Ω_d are:

$$\Omega_a = (1-B)^3; \quad \Omega_b = Z_c - B;$$

$$\Omega_c = (1-B)^2 (B - 0.25); \qquad (6)$$

$$\Omega_d = Z_c - 0.5(1-B)$$

$$B = \frac{1+C_1}{\alpha_c + C_1} \quad \alpha_c - \text{Riedel's criterion} \quad (7)$$

Using experimental values of the critical constants and the acentric factor for the calculation of α_c from the equation:

$$\alpha_c = 5.808 + 4.93\,\omega \qquad (8)$$

the C_1, C_2 and C_3 parameters were obtained by matching points on the saturation curve (vapor pressures together with the corresponding liquid

molar volumes). The C_1, C_2 and C_3 parameters can be obtained by matching only three points on the saturation curve. The objective function for parameters estimation and other details are given elsewhere.[5]

The GEOS3C equation gives exactly the experimental critical point of any substance, and also the experimental critical compressibility factor Z_c. The prediction of liquid volume is improved, without translation, by the parameter C_1 from the temperature function of the attractive term, involved in the B relation (7). The using of three parameters C_1, C_2 and C_3 can represent the saturation pressure curve very good. Finally, the inclusion of the parameter C_1 in the expressions of a and b, leads to a "coupling" between the repulsive and attractive terms in a cubic equation of state.

As pointed out previously,[5] the relations (6-7) are general forms for all the cubic equations of state with two, three and four parameters. This is the meaning of the statement "general cubic equation of state" used for GEOS.

In this work, the coefficients a, b, c, d of eqn. (1) can be obtained for mixtures using the classical van der Waals mixing rules:

$$a = \sum_i \sum_j x_i x_j a_{ij}; \qquad b = \sum_i \sum_j x_i x_j b_{ij}$$

$$(9)$$

$$c = \sum_i \sum_j x_i x_j c_{ij}; \qquad d = \sum_i x_i d_i$$

with

$$a_{ij} = (a_i a_j)^{1/2}(1 - k_{ij}); \quad b_{ij} = \frac{b_i + b_j}{2}(1 - l_{ij}) \quad (10)$$

$c_{ij} = \pm (c_i c_j)^{1/2}$ (with "+" for c_i, $c_j > 0$ and "−" for c_i, $c_j < 0$)

In this work, the binary interaction parameters k_{ij} and l_{ij} were set to zero.

RESULTS AND DISCUSSION

In order to predict accurate values for mixture properties, an equation of state must first be able to properly represent the behavior of pure substances.

The equations of state GEOS3C, SRK, PR, SW and C-1 were tested firstly to calculate equilibrium and thermodynamic properties for R32, R125 and R134a pure fluids, along the saturation curve. The calculations were compared with data of ASHRAE collection.[15] The values of the GEOS3C parameters C_1, C_2 and C_3 for the refrigerants are given in Table 1.

The following thermodynamic properties have been calculated together with the saturation pressure and the two phase densities: compressibility factor, Z; enthalpy, H; enthalpy of vaporization, $\Delta^{vap}H$; entropy, S; heat capacity at constant pressure, C_P; heat capacity at constant volume, C_V; adiabatic index, C_P/C_V; speed of sound, Ws; fugacity coefficient, φ; Joule-Thomson coefficient, JT. The residual thermodynamic properties from the ideal gas at the same temperature and pressure are given

for GEOS in appendix A2 of a previous work.[5] The same relations were used for all EOSs under appropriate restrictions imposed for GEOS parameters (appendix A1[5]). The ideal gas contribution to the thermodynamic properties was calculated using the heat capacity functions recommended in literature.[19]

The results of the calculations for R32, R125 and R134a are summarized in Tables 2-4.

Table 1

Values of critical data[*], acentric factor and C_1, C_2 and C_3 parameters (GEOS3C) for R32, R125 and R134a

Comp.	T_c (K)	P_c (MPa)	$V_c \times 10^3$ (m³/kg)	ω	C_1	C_2	C_3
R32	351.56	5.8579	2.38	0.2710	0.2276	1.1183	-1.7895
R125	339.19	3.5950	1.75	0.3066	0.3408	0.5642	0.1559
R134a	374.18	4.0560	1.95	0.3293	0.3160	0.8256	-0.5629

Critical data and acentric factors from[15]

Table 2

PVT and thermodynamic function deviations on the saturation curve for **R32**. Temperature range (K):215.15 – 351.56. Pressure range (bar): 0.7 – 58.6 . Number of data points: 71

EOS	AAD (%)				AAD (J, mole, K)			
	P^S	V^L	V^V	$\Delta^{vap}H$	H^L	H^V	S^L	S^V
SRK	2.15	30.91	3.72	4.19	568.5	830.9	1.8	2.9
PR	1.49	15.96	2.65	3.40	430.8	690.1	1.4	2.4
GEOS3C	0.41	2.37	2.28	3.38	589.4	535.3	1.9	1.9
C1	1.03	7.37	3.44	4.1	458.4	830.9	1.5	2.9
SW	1.44	18.34	3.08	3.61	379.8	726.8	1.2	2.5

Table 3

PVT and thermodynamic function deviations on the saturation curve for **R125**. Temperature range (K): 203.15 – 339.19. Pressure range (bar): 0.31 – 35.95. Number of data points:71

EOS	AAD (%)				AAD (J, mole, K)			
	P^S	V^L	V^V	$\Delta^{vap}H$	H^L	H^V	S^L	S^V
SRK	1.08	15.54	2.60	4.38	100.5	91.8	0.32	0.56
PR	1.25	4.58	2.90	3.51	87.7	73.1	0.31	0.46
GEOS3C	0.71	2.33	3.96	6.22	137.8	225.6	0.47	0.93
C1	2.63	9.66	4.33	3.89	88.9	77.1	0.31	0.61
SW	1.25	4.44	2.60	3.22	79.4	77.5	0.29	0.46

Table 4

PVT and thermodynamic function deviations on the saturation curve for **R134a**. Temperature range (K): 169.85 – 374.18. Pressure range (bar): 0.0039 – 40.56 . Number of data points: 70

EOS	AAD (%)				AAD (J, mole, K)			
	P^S	V^L	V^V	$\Delta^{vap}H$	H^L	H^V	S^L	S^V
SRK	1.28	18.56	2.92	2.79	380.9	704.8	1.21	2.42
PR	0.80	4.93	2.21	2.19	302.9	464.3	1.03	1.52
GEOS3C	0.26	3.27	1.76	2.28	465.5	223.5	1.54	0.80
C1	1.87	7.90	3.31	2.90	319.0	673.8	1.09	2.31
SW	0.47	5.01	2.13	2.09	219.9	416.3	0.78	1.43

In these tables, the average absolute deviations for a property Y are relative (%):

$$\text{AAD \%}= \frac{\sum_{i=1}^{N}\left|(Y_i^{eos}-Y_i^{\exp})/Y_i^{\exp}\right|\cdot 100}{N} \quad (11)$$

excepting for the enthalpy and entropy where:

$$\text{AAD } H \text{ (or } S) = \frac{\sum_{i=1}^{N}\left|H_i^{eos}-H_i^{\exp}\right|}{N} \quad (12)$$

In each table the number of data points, the pressure and temperature ranges are indicated. The two-phase region properties have been calculated at temperatures from the triple point to the critical point of each substance.

The following observations can be made on the basis of the results for all three pure refrigerants: the vapour pressures and liquid saturated volumes are better represented by GEOS3C, compared to the results obtained using the other equations and the difference in performance between the all EOSs is less noticeable for the other properties.

The equations SRK, PR, SW and C-1 were used with original temperature functions. The same temperature function (eqs. 3-5) with three parameters can be attached to these equations of state. This fact leads to better values for vapor pressures but the values of saturated liquid volumes cannot be improved without a translation procedure.[10] The advantage of the GEOS3C equation is that the prediction of liquid volume is improved without translation by the parameter C_1.[5]

Examples of calculated properties in comparison with experimental data for R134a are presented in Figs. 1, 2 and 3. Fig. 1 shows the saturation curve calculated with the GEOS3C and SRK equations. Figs. 2 and 3 present the enthalpy and the entropy predictions of GEOS3C, SRK, C-1 and SW equations in the saturation range. The GEOS3C equation predicts better the vapor pressure and the saturated liquid volume while the thermodynamic properties are well reproduced by all these EOS.

The capability of all five EOS to reproduce the vapour-liquid equilibrium and the densities of liquid and gas in the single phase region for the refrigerant binary and ternary mixtures containing R32, R125 and R134a was also tested. The classical van der Waals mixing rules without interaction parameters were used. A large comparison with experimental data[15-18] was made. The GEOS3C equation predicts better values for the liquid density for all binary and ternary mixtures, in comparison with the other equations. For the gaseous phase, all equations lead to good predictions of the densities.
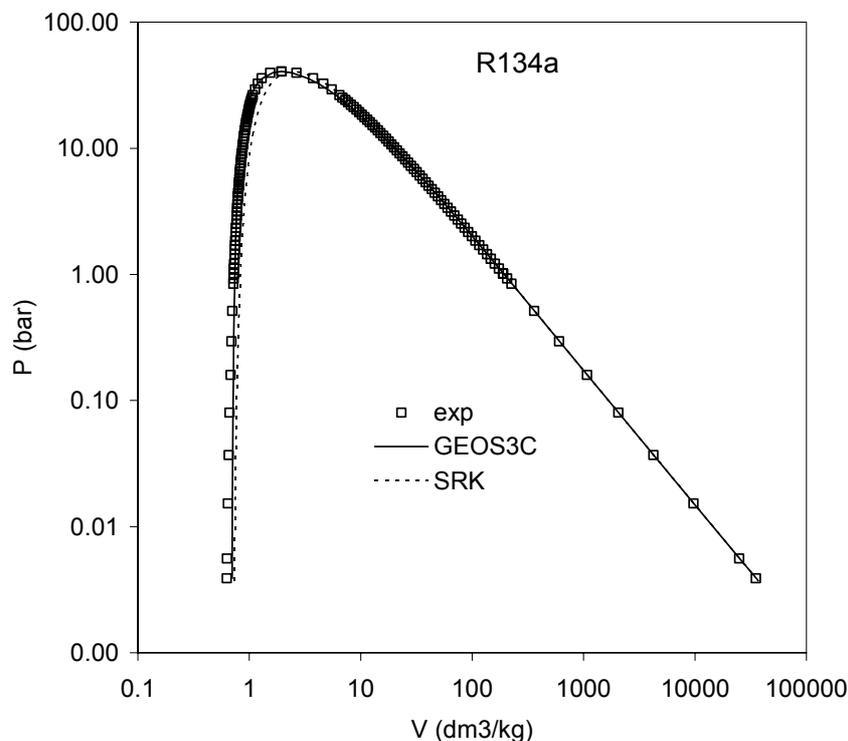

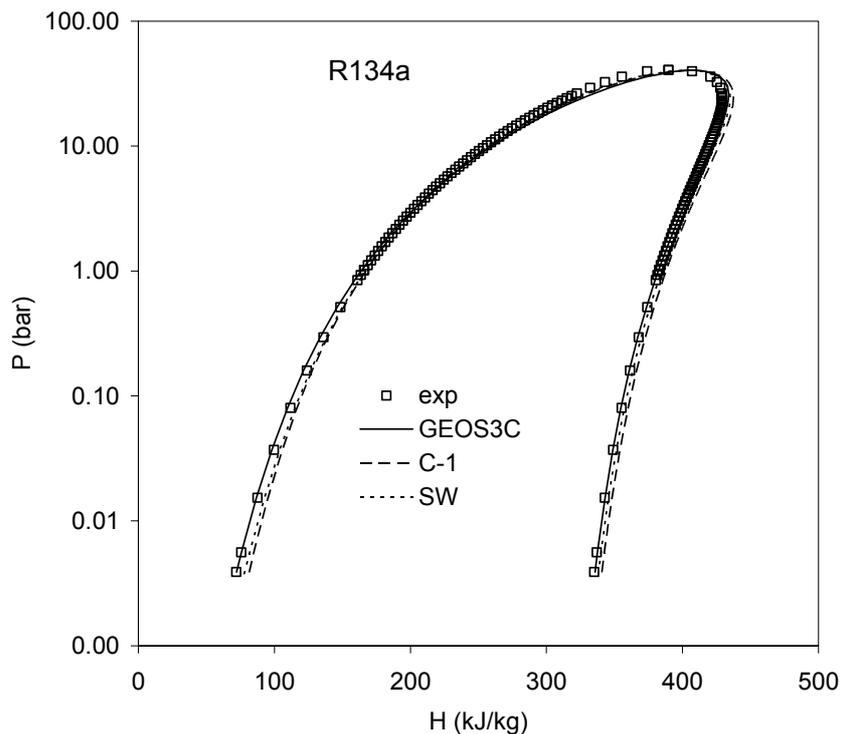Fig. 1 – Pressure-volume diagram for refrigerant R134a.

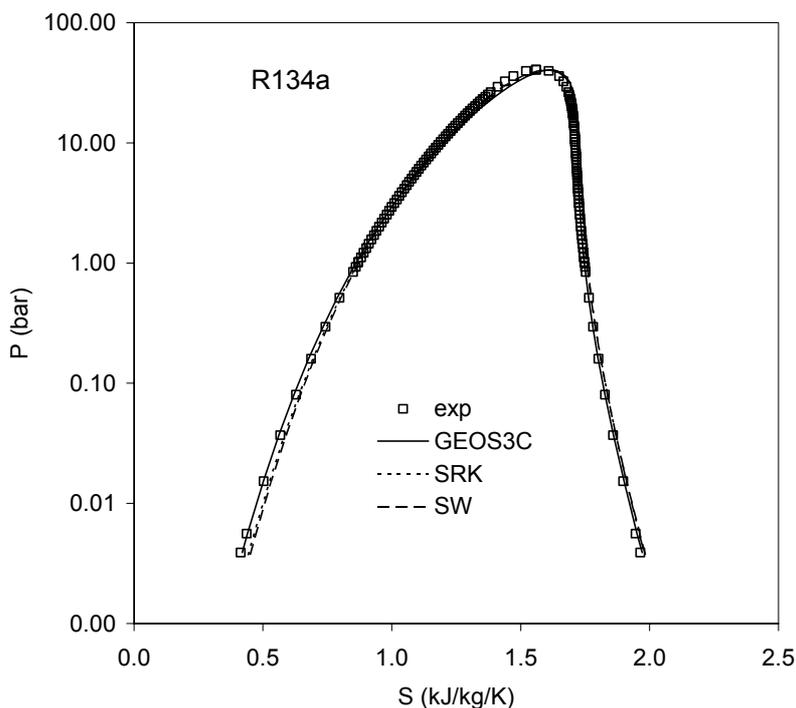Fig. 2 – Pressure-enthalpy diagram for refrigerant R134a.

Fig. 3 – Pressure-entropy diagram for refrigerant R134a.

Some results of the density calculations for the binary mixture R32 + R125 at different pressures and composition, obtained by the GEOS3C equation, for gas in the single phase region, are presented in Fig. 4. The calculations are in good agreement with experimental data.

Examples of deviation calculations using the GEOS3C, SRK and PR equations, for liquid and gas density are presented in Figs. 5 and 6 at constant temperature and composition for R32 + R125 + R134a ternary system. The equations C-1 and SW predict similar values with the PR equation.
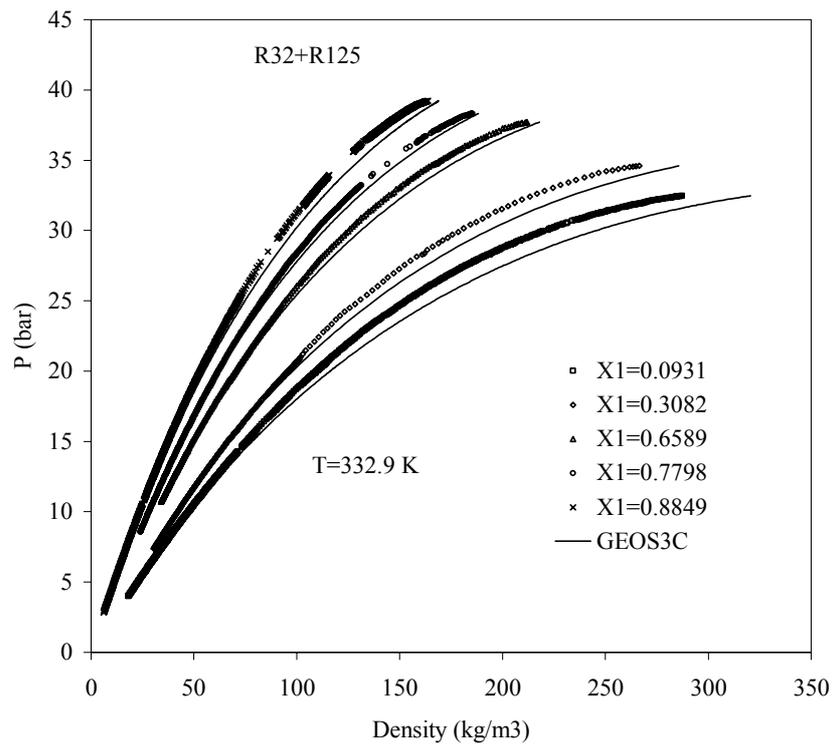
Fig. 4 – The isotherm T=332.9 K for five different composition of the binary mixture
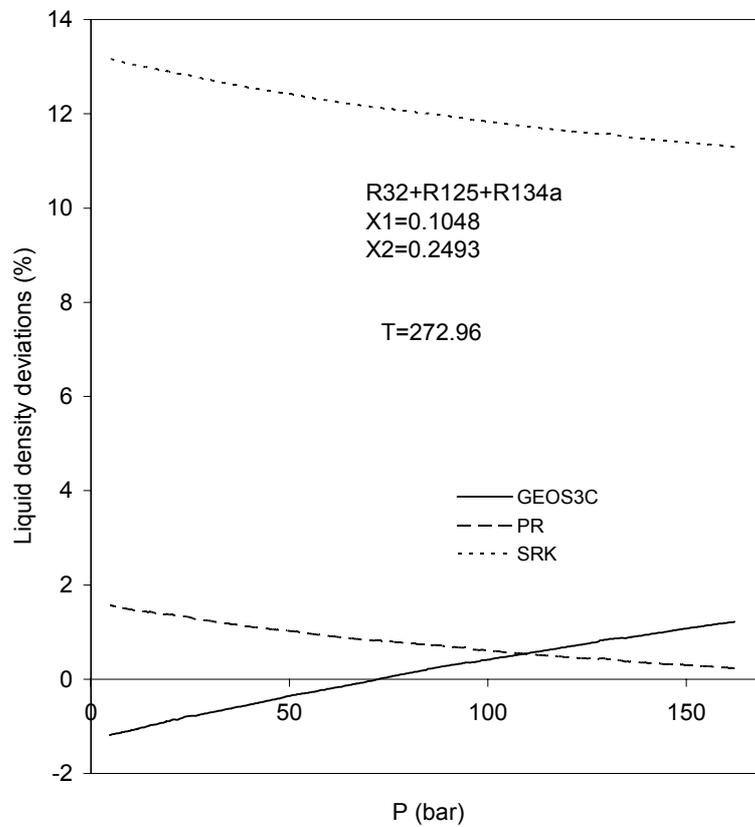R32(1) + R125 (2), gaseous phase.

Fig. 5 – Liquid density deviations for R32 (1) + R125 (2) + R134a (3) ternary system
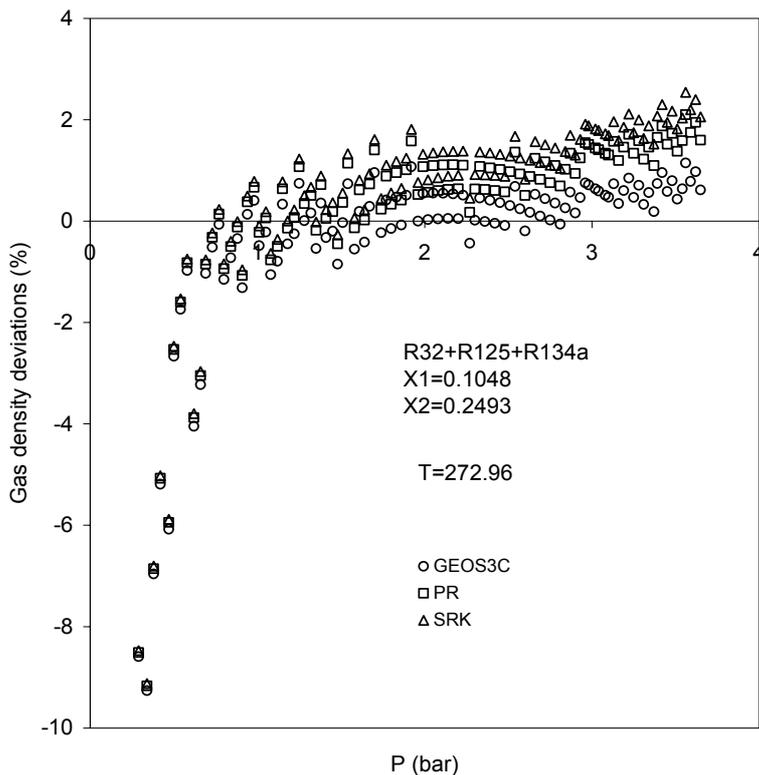at constant temperature and composition.

Fig. 6 – Gas density deviations for R32 (1) + R125 (2) + R134a (3) ternary system at constant temperature and composition.
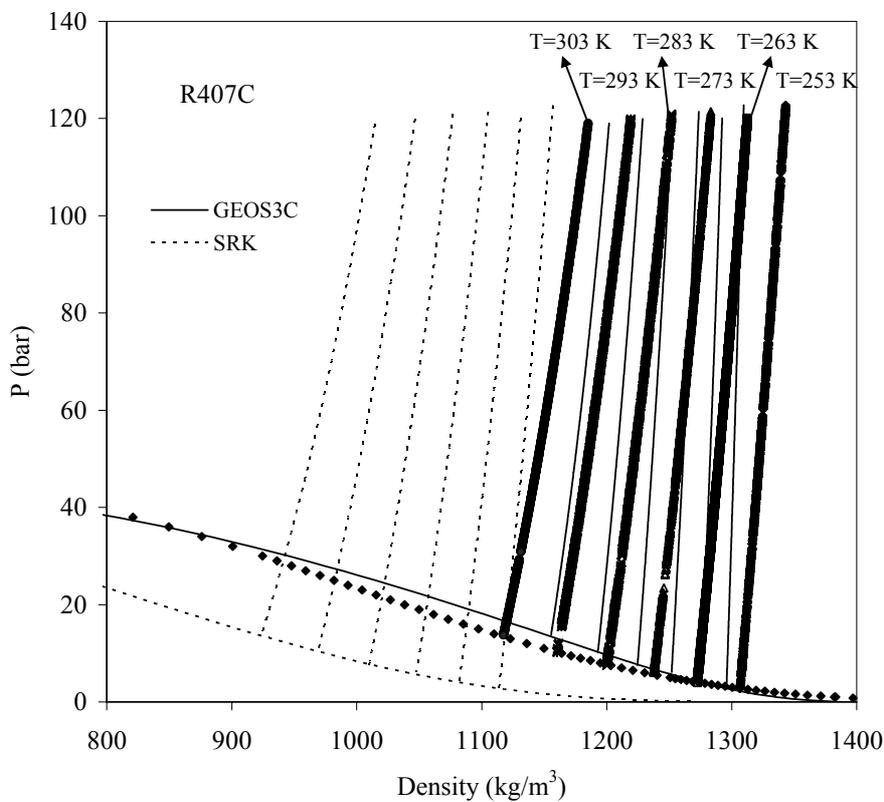

Fig. 7 – Phase equilibrium diagram (bubble curve with six isotherms) for R407C (R32 23% + R125 25% + R134a 52%, wt) ternary system; ◊ (thick lines) experimental points on the saturation curve and isotherms.

The equilibrium diagram for the ternary system, refrigerant R407C [R32 (23%) + R125 (25%) + R134a (52%), wt], bubble point curve with six isotherms, is presented in the Fig. 7. The calculations were performed with the GEOS3C and SRK equations. The agreement with the experimental data is better for the GEOS3C equation. The SRK equation has very large deviations both in bubble point curve and the isotherms.

CONCLUSIONS

Vapour-liquid equilibrium, volumetric and thermodynamic properties were predicted for three pure refrigerants (R32, R125 and R134a) as well as for binary and ternary mixtures of these substances, using the cubic equations of state GEOS3C, SRK, PR, SW and C-1.

The GEOS3C equation with three pure component parameters obtained by matching points on the saturation curve (vapour pressures together with the corresponding liquid volumes) gives the best results for vapour pressure and liquid volume at saturation. The other equations used with the same temperature function with three parameters lead to better values for vapour pressures but the values of saturated volumes can not be improved without a translation procedure. The difference in performance between the three equations is less noticeable for the thermodynamic properties: enthalpy, entropy, enthalpy of vaporization, etc.

For the binary and ternary refrigerant systems, the GEOS3C equation predicts better values of the liquid density. For the gaseous phase, all equations lead to good predictions of the densities.

The use of interaction binary parameters in the classical van der Waals mixing rules does not lead to significant improvement in the calculation of the volumetric and the thermodynamic properties for the studied binary and ternary systems.

List of symbols

a, b, c, d	- parameters in GEOS
AAD	- absolute average deviation
B	- dimensionless parameter in GEOS, defined by eq. (7)

C_1, C_2 and C_3	- parameters in GEOS3C temperature function
C_V, C_P	- isochoric and isobaric heat capacities
H	- enthalpy
JT	- Joule-Thomson coefficient
M	- molar mass
P, P^S	- pressure, saturation pressure
R	- universal gas constant
S	- entropy
T	- temperature
V, V^L, V^V	- molar volume, liquid molar volume, vapor volume
W_S	- speed of sound
Z	- compresibility factor

Greeks

α_c	- Riedel's criterion (parameter in GEOS)
β	- reduced temperature function in GEOS
φ	- fugacity coefficient
Ω_a, Ω_b, Ω_c, Ω_d	- parameters of GEOS
ω	- acentric factor

Subscripts

c	- critical property
r	- reduced property

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